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| REPORT DOCUMENTATION PAGE | | | | Form Approved OMB NO. 0704-0188 | |
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| 1. REPORT DATE (DD-MM-YYYY) 31-03-2013 | | 2. REPORT TYPE Final Report | | 3. DATES COVERED (From - To) 20-Aug-2009 - 19-Dec-2012 | |
| 4. TITLE AND SUBTITLE Discovering, Understanding and Predicting Emergent Phenomena at Strongly Correlated Oxide Interfaces | | | | 5a. CONTRACT NUMBER W911NF-09-1-0415 | |
| | | | | 5b. GRANT NUMBER | |
| | | | | 5c. PROGRAM ELEMENT NUMBER 611102 | |
| 6. AUTHORS David Muller, Darrell Schlom, Craig Fennie | | | | 5d. PROJECT NUMBER | |
| | | | | 5e. TASK NUMBER | |
| | | | | 5f. WORK UNIT NUMBER | |
| 7. PERFORMING ORGANIZATION NAMES AND ADDRESSES Cornell University Office of Sponsored Programs 373 Pine Tree Road Ithaca, NY 14850 -2820 | | | | 8. PERFORMING ORGANIZATION REPORT NUMBER | |
| 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211 | | | | 10. SPONSOR/MONITOR'S ACRONYM(S) ARO | |
| | | | | 11. SPONSOR/MONITOR'S REPORT NUMBER(S) 57222-PH.14 | |
| 12. DISTRIBUTION AVAILABILITY STATEMENT Approved for Public Release; Distribution Unlimited | | | | | |
| 13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation. | | | | | |
| 14. ABSTRACT Transition metal oxides are strongly correlated electron systems, with behavior controlled by subtle compromises between different competing states which gives the oxides a heightened sensitivity to external perturbations, like pressure or applied fields. Our goal here is to develop layered oxide analogs of lattice-matched perovskites that offer increased oxygen stability, higher carrier densities, and an intrinsically reduced dimensionality through a layered internal structure that should help to stabilize emergent interface phenomena resulting from the competition | | | | | |
| 15. SUBJECT TERMS Oxide, MBE, Defect Engineering, TEM, Correlated Electron System | | | | | |
| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT UU | 15. NUMBER OF PAGES | 19a. NAME OF RESPONSIBLE PERSON David Muller |
| a. REPORT UU | b. ABSTRACT UU | c. THIS PAGE UU | | | 19b. TELEPHONE NUMBER 607-255-4065 |

Report Title

ABSTRACT

Transition metal oxides are strongly correlated electron systems, with behavior controlled by subtle compromises between different competing states which gives the oxides a heightened sensitivity to external perturbations, like pressure or applied fields. Our goal here is to develop layered oxide analogs of lattice-matched perovskites that offer increased oxygen stability, higher carrier densities, and an intrinsically reduced dimensionality through a layered internal structure that should help to stabilize emergent interface phenomena resulting from the competition between closely-confined ground states.

We have succeeded in defect-engineering the Ruddlesden-Popper (RP) system to reduce dielectric losses and identified dynamical rearrangements during growth of the RP layers that can be tuned to improve growth quality. Likely other oxide systems, whose performance in thin film form is limited by point defects, could also be greatly enhanced with similar defect engineering. We show that cation defects in LaAlO_3 can control the formation of a two-dimensional electron liquid at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface.

We identify infinite-layer cuprates as a promising materials family for bipolar heterostructure devices in correlated oxide electronics, and grow high quality thin films that allow us to address a long-standing discrepancy in the asymmetry between electron and hole doping in high-temperature cuprate superconductivity.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

| <u>Received</u> | <u>Paper</u> |
|-----------------|--|
| 03/25/2013 | 6.00 John W. Harter, Luigi Maritato, Daniel E. Shai, Eric J. Monkman, Yuefeng Nie, Darrell G. Schlom, Kyle M. Shen. Nodeless Superconducting Phase Arising from a Strong (pi, pi) Antiferromagnetic Phase in the Infinite-Layer Electron-Doped $\text{Sr}_{1-x}\text{La}_x\text{CuO}_2$ Compound, Physical Review Letters, (12 2012): 267001. doi: 10.1103/PhysRevLett.109.267001 |
| 03/25/2013 | 10.00 L. Fitting Kourkoutis, H.L. Xin, T. Higuchi, Y. Hotta, J.H. Lee, Y. Hikita, D.G. Schlom, H.Y. Hwang, D.A. Muller. Atomic-resolution spectroscopic imaging of oxide interfaces, Philosophical Magazine, (12 2010): 4731. doi: 10.1080/14786435.2010.518983 |
| 03/25/2013 | 9.00 Ye Zhu, David A. Muller, Huolin L. Xin. Determining On-Axis Crystal Thickness with Quantitative Position-Averaged Incoherent Bright-Field Signal in an Aberration-Corrected STEM, Microscopy and Microanalysis, (05 2012): 720. doi: 10.1017/S1431927612000189 |
| 03/25/2013 | 8.00 C.-H. Lee, N. J. Podraza, Y. Zhu, R. F. Berger, S. Shen, M. Sestak, R. W. Collins, L. F. Kourkoutis, J. A. Mundy, H. Wang, Q. Mao, X. Xi, L. J. Brillson, J. B. Neaton, D. A. Muller, D. G. Schlom. Effect of reduced dimensionality on the optical band gap of SrTiO_3 , Appl. Phys. Lett., (03 2013): 122901. doi: |
| 03/25/2013 | 7.00 L. Maritato, A. Galdi, P. Orgiani, J. W. Harter, J. Schubert, K. M. Shen, D. G. Schlom. Layer-by-layer shuttered molecular-beam epitaxial growth of superconducting $\text{Sr}_{1-x}\text{La}_x\text{CuO}_2$ thin films, Journal of Applied Physics, (02 2013): 53911. doi: 10.1063/1.4790150 |
| 03/27/2013 | 11.00 Che-Hui Lee, Volodymyr Skoromets, Michael D. Biegalski, Shiming Lei, Ryan Haislmaier, Margitta Bernhagen, Reinhard Uecker, Xiaoxing Xi, Venkatraman Gopalan, Xavier Marti?, Stanislav Kamba, Petr Kuz?el, Darrell G. Schlom. Effect of stoichiometry on the dielectric properties and soft mode behavior of strained epitaxial SrTiO_3 thin films on DyScO_3 substrates, Applied Physics Letters, (03 2013): 82905. doi: 10.1063/1.4793649 |
| 03/31/2010 | 1.00 J. Mannhart, D. Schlom. Oxide Interfaces - An Opportunity for Electronics Science Magazine Vol 327, Science, (03 2010): . doi: |
| 08/05/2010 | 2.00 A. Millis, D. Schlom. Electron-hole liquids in transition-metal oxide heterostructures, Physical Review B, (08 2010): . doi: |
| 08/31/2011 | 3.00 Jochen Mannhart, Darrell G. Schlom. Oxide electronics: Interface takes charge over Si, Nature Materials, (03 2011): 168. doi: 10.1038/nmat2965 |
| TOTAL: | 9 |

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

D.G. Schlom* and K. Shen*, “A Modern Spectroscopic Search for New High Temperature Superconductors,” at Superconductivity 297K! Synthetic Highways To Room Temperature Superconductivity in Almaden, California (2012).

D.G. Schlom, “Why Ruin an MBE? Reflections on a Quarter Century of Oxide MBE,” presented at the 29th North American Molecular Beam Epitaxy Conference in Stone Mountain Park, Georgia (2012). (MBE Innovator Award Lecture)

D.G. Schlom, “Changing Dielectrics into Ferroelectrics—Alchemy Enabled by Strain,” presented at the Electroceramics XIII conference in Enschede, The Netherlands (2012). (Plenary Lecture)

D.G. Schlom, “Utilizing Oxide Interfaces to Getter Point Defects for Improved Tunable Microwave Dielectrics,” presented at the Workshop on Recent Progress in Oxide Interfaces at the Institute of Physics, Chinese Academy of Science in Beijing, China (2012).

C.?H. Lee, N.D. Orloff, T. Birol, Y. Zhu, L. Fitting Kourkoutis, V. Goian, R. Haislmaier, E. Vlahos, M.D. Biegalski, N. Benedek, M. Bernhagen, Y. Kim, J.D. Brock, R. Uecker, V. Gopalan, S. Kamba, X.X. Xi, D.A. Muller, C.J. Fennie, I. Takeuchi, J.C. Booth, and D.G. Schlom*, “Tailoring the Defect Structure of Epitaxial Tunable Microwave Dielectrics for Improved Performance,” presented at the 2012 Lawrence Symposium on Epitaxy in Scottsdale, Arizona (2012). (invited)

C.?H. Lee, N.D. Orloff, T. Birol, Y. Zhu, L. Fitting Kourkoutis, V. Goian, R. Haislmaier, E. Vlahos, M.D. Biegalski, N. Benedek, M. Bernhagen, Y. Kim, J.D. Brock, R. Uecker, V. Gopalan, S. Kamba, X.X. Xi, D.A. Muller, C.J. Fennie, I. Takeuchi, J.C. Booth, and D.G. Schlom*, “Synthesis of Defect-Mitigating Tunable Dielectric Materials with Atomic-Layer Control,” Workshop on Complex Oxide and Multiferroic Thin Film Materials Science, Technologies, and Applications in Tucson, Arizona (2012). (invited)

D.G. Schlom, “Oxide-Based Heterostructures,” presented at the 42nd IEEE Semiconductor Interface Specialists Conference in Washington, D.C. (2011). (invited)

D.G. Schlom, “MBE + ARPES—A Powerful Combination for Creating and Revealing the Electronic Structure of Correlated Oxides,” presented at the International Workshop Functionality from Heterostructures in Obergurgl, Austria (2011). (invited)

D

Number of Presentations: 12.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

| <u>Received</u> | <u>Paper</u> | |
|-----------------|--------------|---|
| 08/31/2011 | 4.00 | Che-Hui Lee, Darrell G. Schlom, David A. Muller, Ye Zhu. Atomic Scale Chemical Mapping in SrO(SrTiO ₃) ₆ Ruddlesden-Popper Thin Film, Microsc. Microanal. 2011. 2011/08/10 00:00:00, . : , |
| TOTAL: | 1 | |

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

| <u>Received</u> | <u>Paper</u> | |
|-----------------|--------------|--|
| 03/27/2013 | 12.00 | M.P. Warusawithan, C. Richter, J.A. Mundy, P. Roy, J. Ludwig, S. Paetel, T. Heeg, A.A. Pawlicki, L. Fitting Kourkoutis, M. Zheng, M. Lee, B. Mulcahy, W. Zander, Ye Zhu, J. Schubert, J.N. Eckstein, D.A. Muller, C.S. Hellberg, J. Mannhart, D. G. Schlom. LaAlO ₃ stoichiometry found key to electron liquid formationat LaAlO ₃ /SrTiO ₃ interfaces, arXiv:1303.5352 (03 2013) |
| 03/30/2013 | 13.00 | TeYu Chien, Lena Fitting Kourkoutis, Jak Chakhalian, Benjamin Gray, Michael Kareev, Nathan P. Guisinger, David A. Muller, John W. Freeland. Visualizing Short Range Charge Transfer at the Interfaces Between Ferromagnetic and Superconducting Oxides, Nature Communications (out to review) (03 2013) |
| TOTAL: | 2 | |

Number of Manuscripts:

Books

| <u>Received</u> | <u>Paper</u> | |
|-----------------|--------------|--|
| TOTAL: | | |

Patents Submitted

Patents Awarded

Awards

Schlom awarded MBE Innovator Award by North American MBE Workshop, NAMBE (2012)

Muller elected Fellow of the American Physical Society March 2012

Muller elected Fellow of the Microscopy Society of America Dec 2012

Graduate Students

| <u>NAME</u> | <u>PERCENT SUPPORTED</u> |
|------------------------|--------------------------|
| FTE Equivalent: | |
| Total Number: | |

Names of Post Doctorates

| <u>NAME</u> | <u>PERCENT SUPPORTED</u> |
|--|--------------------------|
| Ye Zhu | 1.00 |
| Prof Luigi Maritato as a visiting Schola | 1.00 |
| FTE Equivalent: | 2.00 |
| Total Number: | 2 |

Names of Faculty Supported

| <u>NAME</u> | <u>PERCENT SUPPORTED</u> |
|------------------------|--------------------------|
| FTE Equivalent: | |
| Total Number: | |

Names of Under Graduate students supported

| <u>NAME</u> | <u>PERCENT SUPPORTED</u> |
|------------------------|--------------------------|
| FTE Equivalent: | |
| Total Number: | |

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale): 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PhDs

NAME

Total Number:

Names of other research staff

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

see attachment

Technology Transfer

SCIENTIFIC PROGRESS AND ACCOMPLISHMENTS

Taming uncontrolled point defects is the Grand Challenge for making complex oxide films suitable for emerging applications. While ~1% composition control is state-of-the-art, it is often not good enough. A key hypothesis of our approach is that more forgiving oxide systems exist in which to exploit interface phenomena than the widely studied perovskite family. Specifically, we speculated that perovskite-related phases known as Ruddlesden-Popper phases (RP)¹⁻³ would have fewer point defects despite the same ~1% accuracy in our ability to control the stoichiometry of the depositing fluxes. The extensive measurements we have made on RP $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ films support this hypothesis. The accommodation of atomic excesses and deficiencies in the RP layers has led to dramatic improvements in materials properties sensitive to point defects such as the figure merit for tunable dielectrics. However, the increase or decrease in the RP fault length with stoichiometry has also meant a disruption of the planar nature of the interposed film, which impacts transport properties. Thus to construct an oxide system that can have both p-type and n-type conductivity in close proximity to work toward a Bose-Einstein condensate of bound excitons we selected the “infinite-layer” CuO_2 -based phase. This materials system is attractive because (1) both hole-doped and electron-doped variants exist in the “infinite layer” cuprate,^{4,5} (2) the interlayer transport is typically extremely small, and (3) single or bilayers with reasonable hole densities have already been obtained⁶. Even though the electron-doped superconductor $\text{Sr}_{1-x}\text{La}_x\text{CuO}_2$ cannot be synthesized in single-crystal form, IL cuprates can be grown in thin films, but the choice of substrate is critical as substrate strain impacts the properties. We have successfully stabilized layers on GdScO_3 (110). Our SLCO films show peak superconducting transition of 35K at $x \sim 0.1$ (ref⁷). Angle-resolved photoemission reveals a strong coupling between the electrons and the (π, π) ferromagnetism that reconstructs the Fermi surface and leads to a nodeless superconductivity⁸.

In studying the growth of layered oxide compounds, we have gained insight into some fundamental growth mechanisms, including dynamical rearrangements during growth. We identified a surface cation interdiffusion mechanism involving the deposition of Sr-O rock-salt layers in perovskite SrTiO_3 . While SrTiO_3 is normally terminated with a TiO_2 or even double TiO_2 plane, a double SrO layer (i.e. a complete RP fault) appears to be a more stable configuration during growth of Sr-rich films. This preference for $(\text{SrO})_2$ at the surface led to a dynamical exchange of $(\text{SrO})_2$ the next deposited TiO_2 and consequently the disappearance of the first deposited RP plane during the growth of any RP $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ films, for all n . Recognizing the effective surfactant role of the double SrO layer, we could retain the correct structure with rock-salt layers at the desired positions by growing under Sr-rich conditions such that a double SrO layer was always present in RHEED.

With the growth of higher quality RP films, we achieved an experimental realization of a highly tunable ground state arising from the emergence of a local ferroelectric instability⁹ in biaxially strained $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ phases with $n \geq 3$ at frequencies up to 120 GHz. In contrast to traditional methods of modifying ferroelectrics—doping or strain — in this rather unique system increasing the separation between the $(\text{SrO})_2$ planes bolsters the local ferroelectric instability. This new control parameter, n , can be exploited to achieve

a figure of merit at room temperature that rivals all known tunable microwave dielectrics. Of broader importance, however, is the likelihood that a multitude of other oxide systems, whose performance in thin film form is limited by point defects, could also be greatly enhanced with appropriate defect engineering. Exploiting host systems that form planar defects more readily than point defects is clearly advantageous.

POINT DEFECT ENGINEERING IN RP PHASES

We pursued two avenues to test our hypothesis that RP phases would be less accommodating than perovskites to point defects: comparison of the properties of (i) the widely studied $\text{LaAlO}_3/\text{SrTiO}_3$ perovskite interface to its RP analog, $\text{LaSrAlO}_4/\text{Sr}_2\text{TiO}_4$, and (ii) the dielectric loss of SrTiO_3 perovskite films to their RP analogs, $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ phases. Unfortunately, our attempts to realize sharp $\text{LaSrAlO}_4/\text{Sr}_2\text{TiO}_4$ interfaces were stymied by the roughness of the closely lattice matched perovskite substrates we were using and their step heights being different than that of the RP phases we were growing on top of them. Because of these issues, we abandoned approach (i) in favor of approach (ii). Due to the sensitivity of the loss of tunable microwave dielectrics to point defects, RP $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ films were used as a test bed to see if their $(\text{SrO})_2$ crystallographic shear faults in the immediate vicinity of SrTiO_3 perovskite layers, are a useful approach to reduce the point defect concentration in perovskite thin films. As the results below show, the data soundly support our hypothesis.

We grew epitaxial $n = 1$ to 6 $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ films on (110) DyScO_3 and (110) GdScO_3 substrates. X-ray diffraction (XRD) scans of the $n = 1$ to 6 films reveal them to be single-phase and commensurately strained to the substrates upon which they were grown. The θ - 2θ XRD scan of each $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ film shows all expected peaks and would seem to imply perfect layer periodicity along the out-of-plane direction in each sample. Bright-field scanning transmission electron microscope (STEM) images of the $n = 6/\text{DyScO}_3$ sample (Fig. 1a), however, show there are not only periodic horizontal $(\text{SrO})_2$ planes, but also aperiodic vertical $(\text{SrO})_2$ planes. A histogram analysis (Fig. 1b) of the layering disorder reveals that the majority of the layers along the growth direction are comprised of the desired six perovskite layers. The remaining layers have spacings that are harmonics of $n = 6$, i.e., locally $n = 12, 18$, and 24 , that are well lattice matched to the surrounding $n = 6$ matrix. These harmonic n values and vertical $(\text{SrO})_2$ layers likely form to accommodate local stoichiometry variations encountered during growth. Atomic models of the $n = 6$ phase explaining its ability to accommodate local non-stoichiometry are provided in Figs. 1c-f.

The tunable dielectric properties of $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ films were measured through a collaboration with NIST and the University of Maryland and were the subject of Nate Orloff's Ph.D. thesis.¹² His detailed measurements, which span over 8 orders of magnitude in frequency, are shown in Fig. 2 for $n = 3, 4, 5$, and 6 $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ films grown on (110) DyScO_3 . From the measurements in Fig. 2 it is evident that the dielectric constant and tunability of our $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ films are independent of frequency. Measurement of the tunability at MHz frequencies revealed identical values.

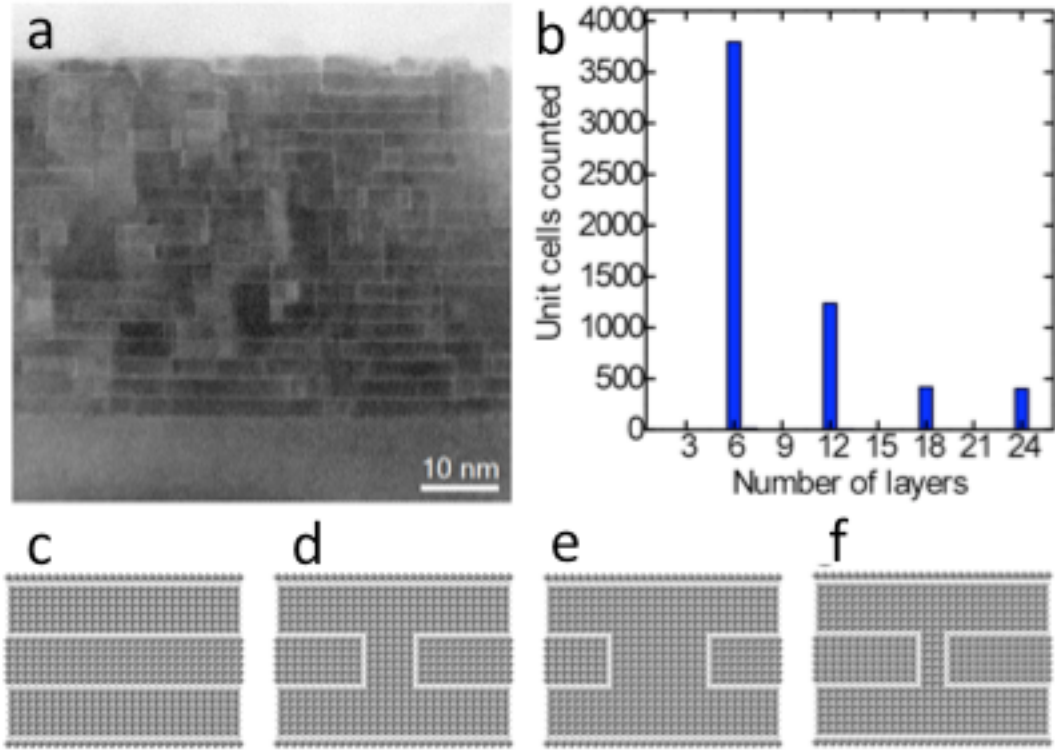


Figure 1: **a** Bright-field TEM image of the $n = 6$ $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ film grown on DyScO_3 . **b**, Histogram of the number of perovskite layers between $(\text{SrO})_2$ layers along the out-of-plane direction. Atomic models of the $n = 6$ phase for local non-stoichiometry accommodation in the case of: **c**, stoichiometric, **d**, stoichiometric despite vertical $(\text{SrO})_2$ layers, **e**, ~12% Sr-poor, **f**, ~7% Sr-rich.

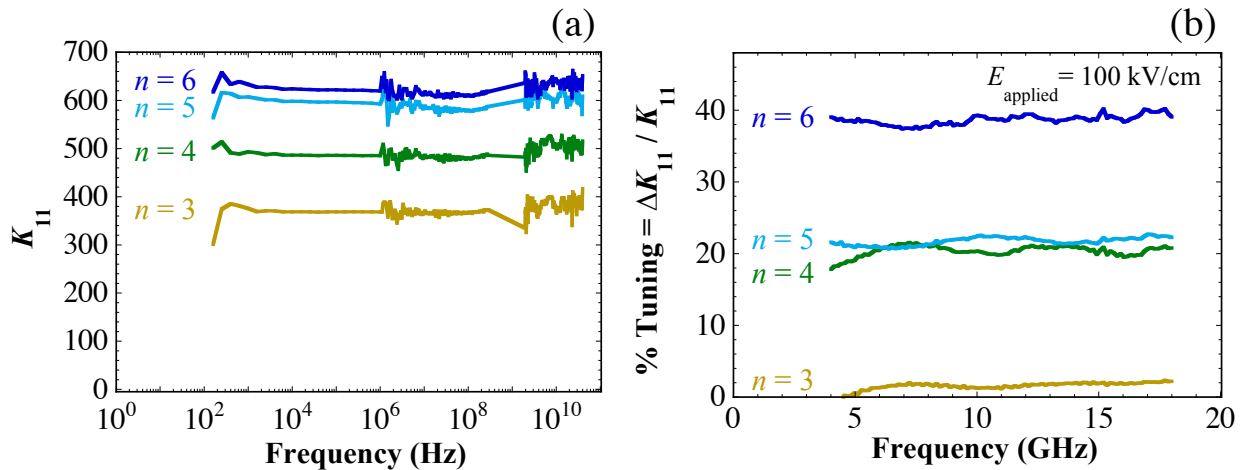


Fig. 2. Room temperature measurements of the frequency dependence of the (a) in-plane dielectric constant (K_{11}) and (b) in-plane tunability of the dielectric constant ($\Delta K_{11}/K_{11}$) through the application of a 100 kV/cm electric field to 50 nm thick $n = 3, 4, 5$, and 6 $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ films coherently strained to (110) DyScO_3 substrates (from Ref. 12,1).

The best fit of the dielectric constant data, which spans over 8 orders of magnitude, is shown in Fig. 3(b) and 3(c) for $n = 3, 4, 5$, and 6 $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1} / \text{DyScO}_3$ films. Measurements on $n = \infty$ $\text{SrTiO}_3 / \text{DyScO}_3$ control samples using these same broadband techniques replicated their high loss and poor figure of merit.¹³ Having fit the loss as a function of frequency, the figure of merit of a tunable dielectric,¹⁴ $\text{FOM} = \left(\frac{\Delta K}{K \tan \delta} \right)$, can then be calculated as a function of frequency. The result is shown in Fig. 2 for our $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1} / \text{DyScO}_3$ films together with the tunable dielectrics with the highest reported figures of merit in the GHz regime from the literature. From Fig. 2(a) it is evident that our $n = 6$ $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1} / \text{DyScO}_3$ film has the highest figure of merit ever reported at room temperature. As the figure of merit exhibits considerable frequency dependence, in Fig. 2(b) we compare the frequency dependence of the figure of merit of our $n = 6$ film with the $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ film with the highest reported figure of merit on which frequency-dependent measurements have been made.¹⁵ The $n = 6$ $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1} / \text{DyScO}_3$ film exhibits a higher figure of merit at all frequencies in the microwave region. This superiority is despite the three times higher electric field used on the $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ film; with higher fields the tunability and thus figure of merit increases. The result points to the possibility of tunable dielectrics with reasonable performance up to 40 GHz, a huge improvement over $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ tunable dielectric films, which have been studied and perfected for decades.

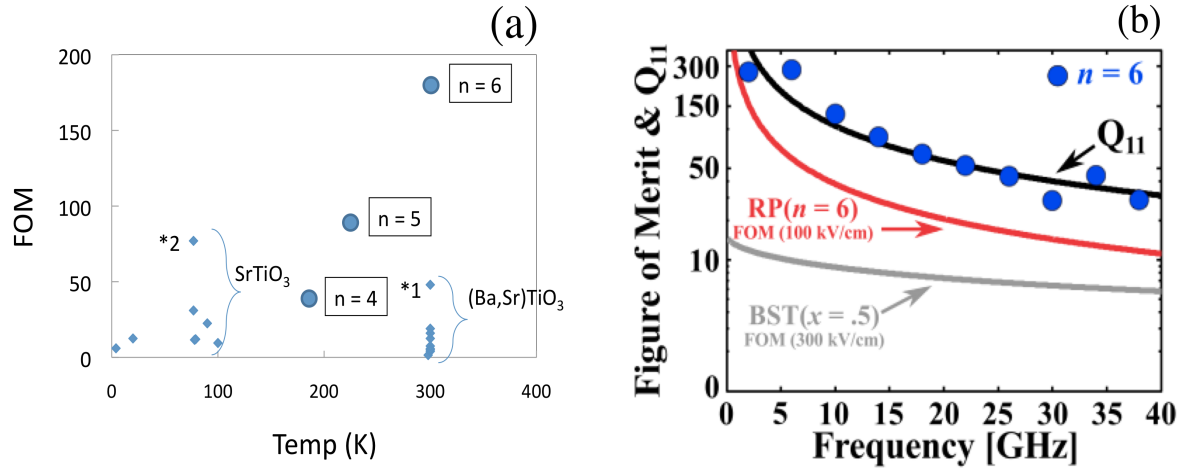


Fig. 3. The figure of merit (FOM) in the GHz regime of tunable dielectrics. (a) FOM as a function of temperature for the best tunable dielectrics. The values plotted are from Table 1 in Ref. 1; *1 is from Ref. 1 and *2 is from Ref. 1. At room temperature the $n=6$ $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ phase, $\text{Sr}_7\text{Ti}_6\text{O}_{19}$, has a figure of merit rivaling any known tunable microwave dielectric material. (b) A comparison of the figure of merit at room temperature of the best $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ film on which frequency-dependent measurements have been reported (Ref. 15) with our 50 nm thick $n = 6$ $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1} / \text{DyScO}_3$ film. The smooth curves are from the fits to both the real and imaginary part of the film dielectric constant as a function of frequency. It is evident that the $n = 6$ $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1} / \text{DyScO}_3$ film is superior over the entire microwave frequency range. This result is due to its much lower loss. The measured values of Q_{11} ($1/\tan \delta_{11}$) of the $n = 6$ film are plotted together with the fit).

EFFECT OF STOICHIOMETRY ON THE DIELECTRIC PROPERTIES AND SOFT MODE BEHAVIOR OF STRAINED EPITAXIAL SrTiO_3 THIN FILMS ON DyScO_3 SUBSTRATES

From the defect engineering studies on RP-phase SrTiO_3 and correlation between point defects and dielectric loss, we proceeded to examine the effect of stoichiometry on the dielectric properties and soft mode behavior of strained epitaxial $\text{Sr}_{1-x}\text{TiO}_{3-\delta}$ films grown on DyScO_3 substrates. Direct comparisons between nominally stoichiometric and non-stoichiometric films were performed through measurements of lattice parameters, temperature-dependent permittivities, second harmonic generation, and terahertz dielectric spectra. The nominally stoichiometric film shows dispersion-free low-frequency permittivity with a sharp maximum and pronounced soft mode behavior. Our results suggest that strained perfectly stoichiometric SrTiO_3 films should not show relaxor behavior and that relaxor behavior emerges from defect dipoles that arise from non-stoichiometry in the highly polarizable strained SrTiO_3 matrix.¹⁶

ROLE OF CATION STOICHIOMETRY IN THE FORMATION OR ABSENCE OF ELECTRON LIQUID PHASES AT THE $\text{LaAlO}_3/\text{SrTiO}_3$ INTERFACE

While we have shown the control of cation stoichiometry can impact the dielectric properties of materials, the next question is how does it impact transport properties? Emergent phenomena, including superconductivity and magnetism, found in the two-dimensional electron liquid (2-DEL) at the interface between the *insulators* LaAlO_3 and SrTiO_3 distinguish this rich system from conventional two-dimensional electron gases at compound semiconductor interfaces. The origin of this 2-DEL, however, is highly debated with focus on the role of defects in the SrTiO_3 while the LaAlO_3 has been assumed perfect. Our experiments and first principles calculations show that the cation stoichiometry of the nominal LaAlO_3 layer is key to 2-DEL formation: only Al-rich LaAlO_3 results in a 2-DEL. While extrinsic defects including oxygen deficiency are known to render $\text{LaAlO}_3/\text{SrTiO}_3$ samples conducting, our results show that in the absence of such extrinsic defects, an interface 2-DEL can form. Its origin is consistent with an intrinsic electronic reconstruction occurring to counteract a polarization catastrophe. This work provides a roadmap for identifying other interfaces where emergent behaviors await discovery¹⁷.

INFINITE LAYER CUPRATES FOR 2D ELECTRON AND HOLE GASES

Having established the validity of our defect engineering hypothesis, we turned to making and measuring the properties of RP systems that could possibly support two-dimensional electron and hole gases in close proximity. The particular RP system that we targeted was La_2CuO_4 and related cuprates. An advantage of the cuprates is that they are known to be able to support both *p*-type and *n*-type conductivity, e.g., Sr-doped La_2CuO_4 is a *p*-type (super)conductor and Ce-doped Nd_2CuO_4 is an *n*-type (super)conductor. These cuprates have been individually studied as doped

superconductors and both have been grown by MBE. We had intended to create two-dimensional electron and hole gases in this RP cuprate in the same heterostructure, with the two-dimensional electron and hole gases in close proximity. We grew Sr-doped La_2CuO_4 films and confirmed that they superconducted.

However, our concerns over vertical faults and disruption of the 2D layer structure by step edges, led us to consider the “infinite-layer” (IL) cuprate compounds instead, i.e., $(\text{Sr}_{1-x}\text{La}_x)\text{CuO}_2$. Again, both hole-doped⁴ and electron-doped⁵ variants exist, and the interlayer transport is typically extremely small. The ACuO_2 infinite layer compounds, where the CuO_2 sheets with four-fold coordinated Cu atoms coordinated by O are separated by A-site cations have the simplest structures of all known superconducting cuprates. Doping is achieved by substitution on the A-sites, e.g. $\text{A}=(\text{Sr}_{1-x}\text{La}_x)$. Despite this simple structure, bulk synthesis has proved challenging, requiring high pressure techniques, and no single crystals of $(\text{A}_{1-x}\text{La}_x)\text{CuO}_2$ exist. The infinite layer cuprates can be grown in thin film form, but the biaxial strain introduced by the substrate plays an important role in determining the Cu-O coordination. In-plane compressive strains (such as from SrTiO_3) degrade the superconducting performance, while in-plane tensile strains give critical temperatures closer to the bulk, polycrystalline values.

We have grown superconducting $\text{Sr}_{1-x}\text{La}_x\text{CuO}_2$ thin films on (110) GdScO_3 substrates by reflection high-energy electron diffraction calibrated layer-by-layer molecular-beam epitaxy⁷. *In-situ* photoemission spectroscopy indicated that the vacuum-annealing step employed immediately after film growth that is critical for achieving superconducting films does so by removing excess oxygen atoms (i.e. the apical oxygens) from the films. The superconducting critical temperature depends on the La content x , with the highest value obtained for $x \sim 0.1$. Resistivity as a function of temperature of optimally doped samples shows a T^2 temperature dependence characteristic of a scattering process where electron-electron interactions dominate.

The quality of the samples allows us to address one of the central issues in high-temperature cuprate superconductivity - the asymmetry between electron and hole doping, where there are apparent discrepancies between the only two known families: $\text{Re}_{2-x}\text{Ce}_x\text{CuO}_4$ which shows antiferromagnetism before d-wave superconductivity sets in, and $\text{A}_{1-x}\text{La}_x\text{CuO}_2$ where a nodeless superconductivity is suggested. Our in-situ angle-resolved photoemission spectroscopy measurements (in collaboration with Kyle Shen) on our epitaxially-stabilized $\text{Sr}_{1-x}\text{La}_x\text{CuO}_2$ thin films reveal a strong coupling between electrons and (π,π) antiferromagnetism that induces a Fermi surface reconstruction which pushes the nodal states below the Fermi level⁸. This removes the hole pocket near (π,π) , realizing nodeless superconductivity without requiring a change in the symmetry of the order parameter and providing a universal understanding of all electron-doped cuprates.

The successful growth and characterization of the infinite-layer cuprates is very encouraging, and this will likely be our target materials family for bipolar heterostructure devices in correlated oxide electronics.

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